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# Energy efficient process for making pyrophyllite-based ceramic tiles using phosphoric acid and mineralizers

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## Abstract

The processing parameters for making ceramic tiles in the pyrophyllite–phosphoric acid binder (P–PA) system have been optimized. The optimized raw material composition requires sintering at a lower temperature of 950 °C. The X-ray powder diffraction studies on the powdered sample of optimized composition have confirmed the presence of dehydroxylate pyrophyllite, tridymite (T-$AlPO_4$), cristyoballite (C-$AlPO_4$) forms of aluminium phosphate and formation of silico-phosphate ($SiP_2O_7$) and alkali aluminium silicates ($NaAlSiO_4$, $KAlSi_3O_8$). The IR studies of the sample show Al–O, Si–O·P–O and Na/K–O linkages. The thermal analysis shows the formation of dehydroxylate pyrophyllite and different forms of $AlPO_4$. Scanning electron microphotograph reveals the chunky morphology of the dehydroxylate pyrophyllite, the rhombohedral morphology of T-$AlPO_4$ and spherical C-$AlPO_4$ and silico-phosphate particles.

*Keywords:* A. Firing; Pyrophyllite; Phosphoric acid; Ceramic tiles; Impact strength; Characterization

## 1. Introduction

The requirement for the sintering of green bodies of ceramics at high temperatures for obtaining desired characteristics in the finished products makes the ceramic manufacturing industry a highly energy-intensive one [1–7]. The studies on the effect of the use of alkali and alkaline earth metal compounds as flux materials have shown that the addition of flux reduces the sintering temperature to an extent [8–11] and also improves the mechanical strength of ceramic bodies [12,13]. In order to achieve considerable lowering in the sintering temperatures, use of various phosphatic binders has been tried and found to be effective [14–19]. Pyrophyllite clay mineral has been found to be a potential material for multifarious applications [20,21]. As pyrophyllite contains silica and alumina in an optimum ratio required for making ceramic wares [14] and has a low coefficient of thermal expansion and a reduced moisture expansion it has been used for making ceramic tiles [22–25]. The phosphate bonding of ceramic bodies involves reaction of the aluminum content present in the raw material with the phosphatic content of the phosphate binders and leads to the formation of various forms of aluminum phosphate at a significantly lower temperature as compared to conventional silicate bonding of ceramic manufacturing [26–29]. For example, when sodium hexa-meta phosphate [15] or di-sodium hydrogen phosphate [16] are used as binder, the crystals of reinforcing T-$AlPO_4$ species formed at a low temperature of sintering of 950 °C provide the required impact strength in the tile bodies. In the present study, the process parameters for making pyrophyllite based ceramic tiles using phosphoric acid as binder have been optimized. The structural transformations taking place during sintering in the optimized composition have been studied using X-ray diffraction, IR spectroscopy, thermal analysis and scanning electron microscopy. The results of these studies are presented in this paper.

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## 2. Experimental procedure

### 2.1. Raw materials and chemicals

Pyrophyllite mineral collected from Khari mines of Tikamgarh district of Madhya Pradesh, India was used in the present studies. The X-ray diffraction studies had confirmed it to be two-layer monoclinic pyrophyllite [14]. The chemical composition of the pyrophyllite mineral is shown in Table 1.

The mineral lumps were powdered and sieved using standard BSS sieves to obtain fractions of desired size (−75 to +45) μm for experimental work. L.R. grade phosphoric acid (sp. gr. 1.85), sodium carbonate and potassium carbonate of Loba India make was used as binder.

### 2.2. Preparation of ceramic tiles

The green tile bodies, were prepared by homogenizing pyrophyllite powder with phosphoric acid (binder) in the required quantity (5–10%, w/w) in a ball mill, humidified and then compacted in a steel mould of dimension 10.2 cm × 10.2 cm × 0.4–0.6 $\text{cm}^3$ using a hydraulic press of 100 ton capacity. Unless specified, the tiles were compressed using pyrophyllite powder having 80% material of (−63 to +45) μm and 20% (−75 to +63) μm size at a pressure of $2.3 \times 10^6$ $\text{kg/m}^2$ for 2.0 min. The compacted tile bodies were dried in an air oven at 110 °C for a period of 2 h. The dried green bodies were place in an electric muffle furnace and its temperature was increased to the required firing temperature at a rate of 15 °C/min. The tiles were soaked at this temperature for 2–4 h where after the furnace was switched off and the tile bodies were furnace cooled to ambient temperature.

### 2.3. Testing of sintered tiles

The sintered ceramic tiles were tested for their impact strength and porosity by water absorption measurements following the procedure laid down in the specifications drawn for ceramic tiles [30]. The ceramic tiles made using optimized composition were found to pass the specifications. The bulk density determination has been performed as per the standard procedure prescribed for ceramics [31]. The procedure for measuring impact strength involved use of falling weight type instrument. The impact strength test was carried out by placing the bottom surface of the tile on a 60 mm equilateral triangular support. A steel ball of 30 g weight was allowed to drop on the top surface, form an initial height of 25 cm. The height of free fall of the steel ball was increased in small increments till failure. Impact strength was calculated as per the formula.

Table 1
Chemical analysis of pyrophyllite clay mineral

| Constituents | Weight percent |
|---|---|
| $SiO_2$ | 64.3 |
| $Al_2O_3$ | 23.90 |
| $Fe_2O_3$ | 2.10 |
| $TiO_2$ | 0.98 |
| MgO | 0.80 |
| CaO | 1.70 |
| $K_2O$ | 0.40 |
| $Na_2O$ | 0.10 |
| L.O.I | 5.60 |

$$\text{Impact strength} = \frac{Wh}{t},$$

where, $W$ = weight of the steel ball in (kg), $h$ = height of free fall of steel ball in (meter), $t$ = thickness of tile in (cm).

### 2.4. Optimization of processing parameters

To optimize the different processing parameters for making ceramic tiles based on the pyrophyllite–PA system, the effects of binder (PA) content (with and without 2.5% $Na_2CO_3$ + 2.5% $K_2CO_3$, w/w), at the particle size of the pyrophyllite powder, pressure and time of compaction of the sintering temperature and of the soaking time on the impact strength and bulk density of the ceramic bodies were investigated.

### 2.5. Studies on phase transformation on the optimized composition

The structural transformations taking place during sintering of the optimized pyrophyllite–PA system were investigated using X-ray diffraction, thermal analysis, infrared spectroscopy and scanning electron microscopy techniques.

X-ray powder diffraction study of the sintered tile sample made using optimized process parameters was carried out using Philips X-ray diffractometer (model No. 1710) with Ni-filtered Cu Kα radiation. The thermal phase transformation in the optimized composition mix was studied using a Stanton Red croft, thermal analyzer (model No. 720) at a heating rate of 10 °C/min. The IR spectra of the samples were recorded in the wave number range of 400–4000 $\text{cm}^{-1}$ using a Perkin Elmer, Infra Red spectrophotometer (Model No. 983G) in KBr. The morphology of the various phases formed in the powdered sample of tile made using optimized process parameters was studied using JEOL make (model No. JEM-35-CF) scanning electron microscope.

## 3. Results and discussion

### 3.1. Effect of binder content

The effect of the binder (PA) content (with and without $Na_2CO_3$ + $K_2CO_3$, each 2.5%, w/w) on the impact strength, bulk density and porosity of the tile bodies made from the pyrophyllite–PA system sintered at 950 °C for 3 h is given in

Table 2
Effect of binder content on impact strength, bulk density and porosity of sintered tile bodies soaked at 950 °C for 3 h

| Compositions | A | B | C | D |
|---|---|---|---|---|
| PA content % (w/w) | 5 | 10 | 5 | 10 |
| $Na_2CO_3$ | – | – | 2.5 | 2.5 |
| $K_2CO_3$ | – | – | 2.5 | 2.5 |
| Impact strength ($J/m^2$) | $1.50 \pm 0.20$ | $1.70 \pm 0.20$ | $1.80 \pm 0.10$ | $2.20 \pm 0.20$ |
| Fired bulk density ($g/cm^3$) | 1.70 | 2.07 | 1.94 | 2.24 |
| Porosity (percent water absorption) | 25.24 | 23.62 | 20.22 | 10.28 |

The green bodies were compacted at $2.30 \times 10^6$ kg/m$^2$ pressure for 2 min.

Table 2. The pyrophyllite powder used in these experiments consisted of 80% (w/w) powder of (−75 to +45) μm and 20% (w/w) of (−75 to +63) μm size. On gradually increasing the binder content from 5 to 10% (w/w), an increase in impact strength is observed. However, a further increase in binder content beyond 10% (w/w) resulted in the sticking of the raw material mix to the steel mould during compaction and hence the effect of >10% $H_3PO_4$ content could not be investigated. Since addition of alkali metals and specially of mixture of alkali metal mineralizers [13] have been found to improve the sintering characteristics of pyrophyllite [32], the addition of 2.5% $Na_2CO_3$ + 2.5% $K_2CO_3$ to pyrophyllite–PA system containing 5 and 10% (w/w) phosphoric acid was tried. These additions led to an increase in the impact strength of tiles to the value of 1.80 and 2.20 J/m$^2$, respectively. These observations are further supported by increase in bulk density and decrease in porosity of the tiles made using these compositions. The maximum bulk density and impact strength is found in the composition containing 2.5% $Na_2CO_3$ + 2.5% $K_2CO_3$ and 10% (w/w) phosphoric acid and the rest 85% (w/w) pyrophyllite. Since a further increase of fluxing agent did not improve the impact strength, bulk density and porosity, the quantity of PA binder (10%, w/w) and fluxing agent (2.5%, w/w) of each, i.e. sodium and potassium carbonate was considered to be optimum for this system.

### 3.2. Effect of particle size of pyrophyllite

The particle size distribution in the compaction mix is known to have a significant influence on densification and microstructure development in the sintered body. To study its effect, the pyrophyllite powder was classified in (−63 to +45) μm and (−75 to +63) μm sizes. The pyrophylite mix powder was prepared by varying the finer particle size content from 75 to 85% (w/w) with coarse fraction making up the rest. The sintered tiles made from the mixed powder pyrophyllite samples (85%, w/w) with 10% (w/w) PA and 2.5% (w/w) each of $Na_2CO_3$ and $K_2CO_3$ were tested for their impact strength, dry and fired bulk density and the results are given in Table 3. It is observed that the tiles made from pyrophyllite powder mixture containing 75% (w/w) powder of (−63 to +45) μm and 25% (w/w) of (−75 to +63) μm size posses an impact strength of (1.90 J/m$^2$), dry bulk density (1.65 g/cm$^3$) and fired bulk density (1.80 g/cm$^3$). An increase in the finer powder content to 80% (w/w) causes improvement in the impact strength value, dry bulk density and fired bulk density. However no further improvement in these properties could be obtained by increasing the content of finer fraction to 85%. Hence the powder mix containing 80% (w/w) powder of (−63 to +45) μm and 20% (w/w) of (−75 to +63) μm size was considered to be optimum and used in further studies.

### 3.3. Effect of compaction pressure

The pressures of $2.0 \times 10^6$, $2.3 \times 10^6$ and $2.5 \times 10^6$ kg/m$^2$ were tried for optimizing the compaction pressure needed for making green tile bodies from 85% (w/w) pyrophyllite + 10% (w/w) PA and 2.5% (w/w) each of $Na_2CO_3$ and $K_2CO_3$. It was observed that the green tile bodies made at a compaction pressure of $2.0 \times 10^6$ kg/m$^2$ did not posses sufficient green strength and crumbled during handling (cf. Table 4). On increasing the compaction pressure to $2.3 \times 10^6$ kg/m$^2$, the tiles made could be dried and sintered successfully. A further increase in compaction pressure to $2.5 \times 10^6$ kg/m$^2$ led to sticking of the raw mix to the surface of steel moulds. Hence a pressure of $2.3 \times 10^6$ kg/m$^2$ was considered to be optimum and used for compaction of tiles for further studies.

### 3.4. Effect of compaction time

To study the effect of compaction time on dry bulk density of unfired tile samples and fired bulk density and impact strength of the sintered tiles, the green bodies of the optimized composition were compacted at the optimized pressure of $2.3 \times 10^6$ kg/m$^2$ for a duration of 30, 60, 120 and

Table 3
Effect of particle size of pyrophyllite powder on impact strength, dry and fired bulk density of sintered tile bodies

| Particle size | | | |
|---|---|---|---|
| (−63 to +45) μm | 75% | 80% | 85% |
| (−75 to +63) μm | 25% | 20% | 15% |
| Impact strength ($J/m^2$) | $1.90 \pm 0.10$ | $2.20 \pm 0.10$ | $2.20 \pm 0.10$ |
| Dry bulk density ($g/cm^3$) | 1.65 | 1.82 | 1.82 |
| Fired bulk density ($g/cm^3$) | 1.80 | 2.24 | 2.23 |

Table 4
Effect of compaction pressure and time on impact strength, dry and fired bulk density of sintered tile bodies

| Compaction pressure (kg/m$^2$) | $2.0 \times 10^6$ | $2.3 \times 10^6$ | | | $2.5 \times 10^6$ |
|---|---|---|---|---|---|
| Impact strength (J/m$^2$) | Green strength was very poor | $2.0 \pm 0.10$ | $2.20 \pm 0.20$ | $2.20 \pm 0.10$ | Raw materials mix stick to the wall of the steel mould |
| Compaction time (in seconds) | – | 60 | 120 | 180 | – |
| Dry bulk density (g/cm$^3$) | – | 1.72 | 1.88 | 1.88 | – |
| Fired bulk density (g/cm$^3$) | – | 1.82 | 2.24 | 2.21 | – |

180 s (cf. Table 4). The green bodies compressed for 30 s had poor green strength and could not be processed further. The green bodies compressed for 60 s yielded tile sample having dry bulk density 1.72 g/cm$^3$, fired bulk density 1.82 g/cm$^3$ and impact strength 2.0 J/m$^2$, respectively. The green bodies compressed for 120 s yielded tile sample having dry bulk density 1.88 g/cm$^3$, fired bulk density 2.24 g/cm$^3$ and impact strength 2.20 J/m$^2$, respectively. Thus, it is observed that the increase in compaction time from 60 to 120 s improves the green and fired properties of the tile bodies. However a further increase in the compaction time to 180 s did not exhibit any further improvement in these properties, therefore it is inferred that a compaction time of 120 s is optimum to obtain tile bodies possessing satisfactory green and fired strength.

### 3.5. *Effect of sintering temperature and soaking time*

To optimize the temperature and soaking time required for the sintering of green tile samples made by compression of optimized composition at $2.3 \times 10^6$ kg/m$^2$ for 120 s, the samples were sintered at 900, 950 and 1000 °C for a period of 2–4 h. The results are shown in Fig. 1. The tiles sintered for 2 h at 900, 950 and 1000 °C had relatively low value of fired density and impact strength compared to values obtained at 3 h soaking time and failed to achieve the desired minimum impact strength (2.0 J/m$^2$). An increase in the soaking time to three hours led to a gradual improvement in the fired density and impact strength. The samples sintered at 950 °C for 3 and 4 h and at 1000 °C for 3 h showed fired bulk density of 2.18–2.24 g/cm$^3$ and an impact strength of 2.20 J/m$^2$. However, the sample sintered at 1000 °C for 4 h had a decrease in fired bulk density of 1.83 g/cm$^3$ and impact strength of only 1.30 J/m$^2$. Hence sintering temperature of 950 °C and soaking time of 3 h was considered to be optimum.

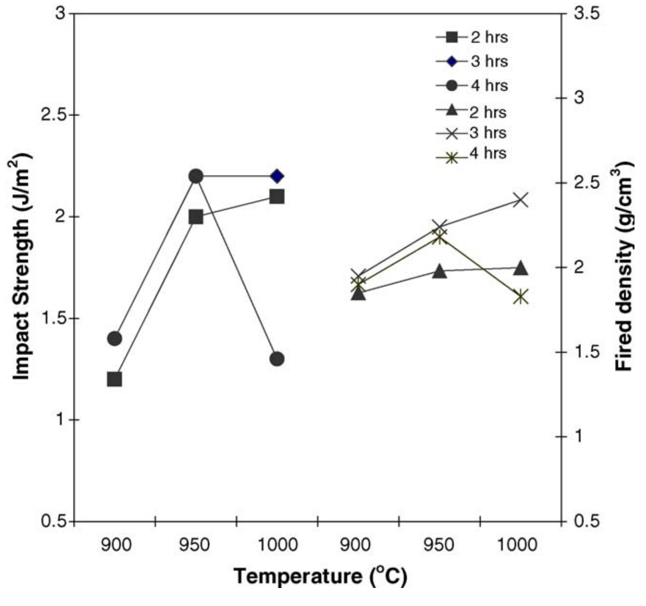

Fig. 1. Effect of sintering temperature and soaking time on impact strength (J/m$^2$) of the sintered tile bodies in the P–PA system.

### 3.6. *Optimized process parameters*

Based on the above results, the optimum composition and processing parameters can be summarized as follows: Composition: pyrophyllite = 85% {particle size: (−75 +63) μm = 20%: and (−63 to +45) μm = 80%, w/w}; PA = 10%; sodium carbonate 2.5% and potassium carbonate 2.5% (w/w). Compaction pressure and duration: $2.3 \times 10^6$ kg/m$^2$ for 120 s; sintering time and duration: 950 °C for 3 h. The tiles prepared using above optimized parameters had fired bulk density = $2.24 \pm 0.06$ g/cm$^3$, percent water absorption = $10.28 \pm 1.30$ and impact strength = $2.20 \pm 0.1$ J/m$^2$.

### 3.7. *Studies on phase transformation in sintered body prepared using optimized process parameters*

#### 3.7.1. *X-ray powder diffraction study*

The X-ray studies of the tiles made using optimized conditions confirms [33] the presence of dehydroxylate pyrophyllite (peaks with '*d*' values 3.10, 4.59 and 4.48 Å) as the major phase. The next major phase observed to be present is the tridymite form of aluminum phosphate (T-$AlPO_4$) (peaks with '*d*' values 4.33, 4.12, 3.68 and 2.87 Å). Small amount of C-$AlPO_4$ is also observed to be present (peaks with '*d*' values 3.80 and 3.01 Å) and also, the formation of silico-phosphate phase is confirmed (peaks with '*d*' values 3.72, 3.34 and 3.24,3.04, 2.09 and 1.98 Å). Similarly the formation of alkali aluminium silicates namely sodium aluminium silicate (peaks with '*d*' values 4.23, 2.59, 2.11, 1.83 and 1.68 Å) and potassium aluminium silicate (peaks with '*d*' values 3.31, 3.77, 4.22, 3.24, 2.99, 2.90, 2.57 and 2.16 Å) has also been confirmed.

#### 3.7.2. *Thermal studies*

The DTA and TGA curves obtained for the tiles made using optimized conditions are shown in Fig. 2. The DTA curve shows the presence of a shallow endothermic peak at

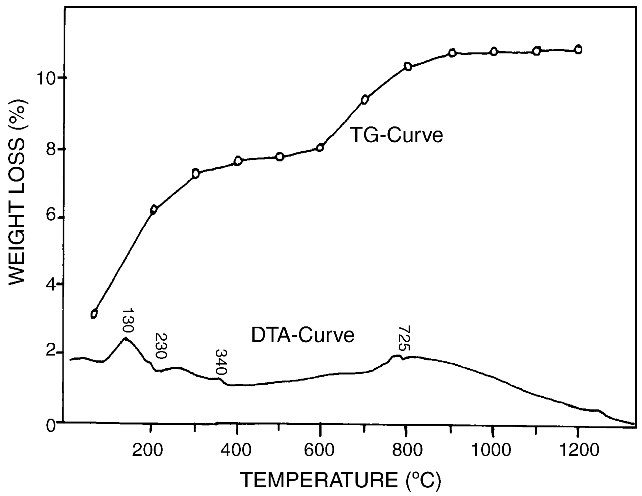

Fig. 2. DTA–TG curve of optimized composition in P–PA system.

about 130 °C, which can be ascribed to the removal of moisture. It is followed by a small endothermic kink at 175 °C corresponding to the formation of mono-aluminium phosphate. The next, two small endothermic peaks at 230 and 340 °C are assigned to the formation of aluminium pyrophosphate and aluminum metaphosphate, respectively [14]. The presence of an endothermic peak at 725 °C may be ascribed to the formation of tridymite form of aluminium phosphate (T-$AlPO_4$) along with some cristobalite form of C-$AlPO_4$. The broad endothermic effect in the temperature range of 600–900 °C may correspond to the dehydroxylation of pyrophyllite. In the temperature range of 950–1100 °C the pyrophyllite dehydoxylate decomposes into Si-rich amorphous phase [34] and the formation of silico-phosphate occurs as a reaction product of silicate compounds with phosphoric acid [34,35]. The TGA curve shows that there is a major and rapid weight loss of 6.35% between ambient to about 200 °C attributable to the removal of moisture and release of structural water molecules from the mono aluminium phosphate. Between 300 and 600 °C, a marginal weight loss of 0.65% is observed, as no further dehydration takes place in the aluminium phosphate system. Similar observation has also been reported by Chen et al. [36]. The observed weight loss of 2.90% between 600 and 900 °C may be ascribed to the formation of dehydroxylate pyrophyllite. These results strengthen the results of X-ray diffraction and IR studies.

### 3.7.3. IR studies

The IR spectra of natural pyrophyllite sample and the powered tile sample prepared under optimized processing parameters (sintering at 950 °C) are given in Figs. 3 and 4, respectively.

The IR spectra of natural pyrophyllite sample (cf. Fig. 3) show the characteristic [37] bands of high intensity at peaks values 489, 539, 813,834, 853, 1046 and 1120 $cm^{-1}$. Other characteristic peaks are observed at 950 and 3675 $cm^{-1}$, which are assigned to the in plane OH vibration [38] and to the $Al_2OH$ stretching mode (interaction between OH and Al [39]. The peak at 1046 $cm^{-1}$ is assigned to Si–O linkage and is characteristic of alumino-silicates. The peak at 949 $cm^{-1}$ is assigned to the Al–(OH) and Si–O linkage. On heating pyrophyllite in the presence of phosphoric acid under optimized conditions of tile making, the various peaks corresponding to Al–O linkages disappeared and new peaks with four fundamental vibrations [40] of orthophosphate at 1082, 980, 515 and 363 $cm^{-1}$ wave numbers are observed (cf. Fig. 4). In addition to peaks of phosphate the characteristic bands of silica at 485 and 801 $cm^{-1}$ and also very weak bands [31] at 992 and 1008 $cm^{-1}$ for Na–O and

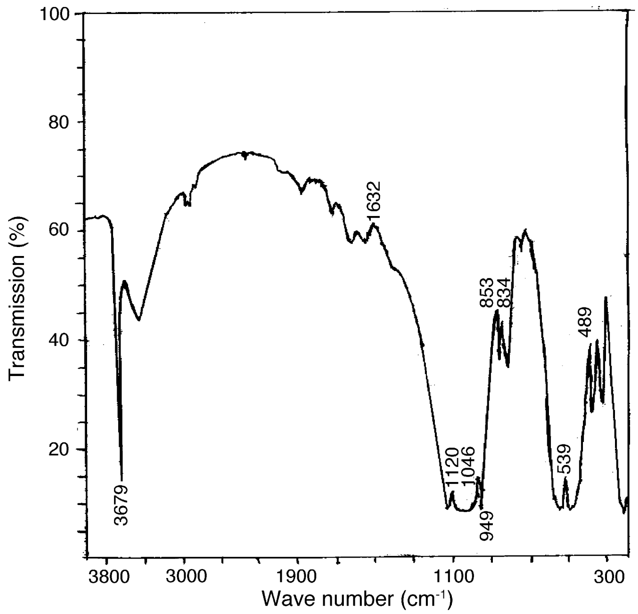

Fig. 3. IR Spectra of natural pyrophyllite mineral.

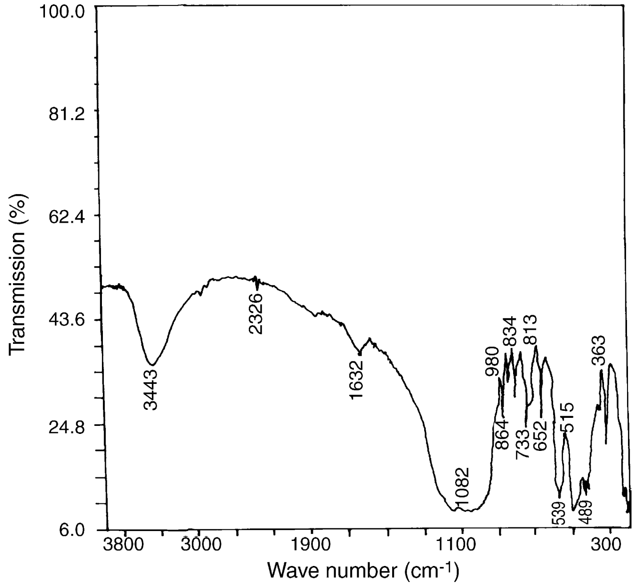

Fig. 4. IR spectra of optimized composition in P–PA system sintered at 950 °C.

K–O linkages are observed [41], which further supports the findings of the X-ray diffraction studies.

### *3.7.4. Morphology of optimized composition of sintered tile body*

The SEM micrograph of the tiles made using optimized conditions (cf. Fig. 5a and b) shows the presence of three types of morphologies: (1) the large size (>10 μm) foliated chunky dehydroxilated pyrophyllite (2) rhombohedral shaped crystals (5–10 μm) of T-$AlPO_4$ and (3) small size spherical particles corresponding to brittle C-$AlPO_4$, silico-phosphate and glassy alkali aluminium silicate phases.

From the above experimental studies, it is inferred that the rhombohedral crystals of T-$AlPO_4$ provide strength to the sintered tile bodies. Since the sintering for longer duration and at higher temperature causes conversion of T-$AlPO_4$ to C-$AlPO_4$, and formation of silico-phosphate phase, the tile sample sintered at 1000 °C for 4 h has a lower impact strength (1.30 $J/m^2$) as compared to the samples sintered at 1000 °C for 3 h and 950 °C for 3 and 4 h. Similar observation have also been made by Cassidy [35], Warrier et al. [19] and Marghussian et al. [34].

## 4. Conclusions

Based on the results of present studies, the following conclusions can be drawn:

1. The ceramic tiles made using the optimized processing parameters in the pyrophyllite–phosphoric acid system confirm to the requirement of impact strength as specified for standard of ceramic tiles ($\geq$2.0 $J/m^2$)
2. The ceramic tiles in the pyrophyllite–PA system using optimized processing parameter can be made by sintering at a significantly lower temperature of 950 °C.
3. The rhombohedral shaped T-$AlPO_4$ crystals act as reinforcement to provide mechanical strength.
4. The observed loss in mechanical strength of tiles on sintering either at higher temperature or for longer duration at lower temperature, has been ascribed to the formation of silico-phosphate phase.
5. The presence of four fundamental vibration ascribed to aluminium phosphates in IR spectra, further support the thermal studies and finding of XRD.

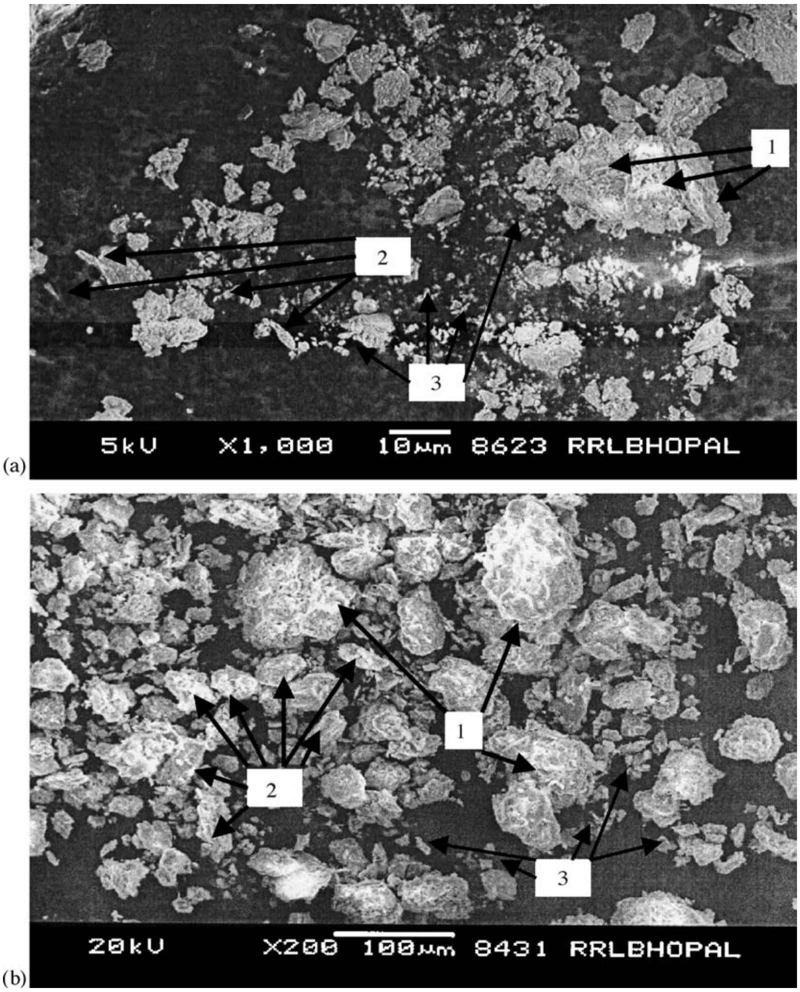

Fig. 5. (a and b) SEM micrograph of optimized composition in P–PA system sintered at 950 °C for 2 h: (1) dehydroxylated pyrophyllite, (2) rhombohedral crystals of T-$AlPO_4$ and (3) C-$AlPO_4$.

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